Chapter 7
PCBs/trans-Nonachlor in the Lower Pelagic Food Web

7.1 Results

The lower pelagic food web was sampled from June 1994 through October 1995 for PCB and *trans*-nonachlor analysis. Individual samples of the lower pelagic food web included mixed phytoplankton, mixed zooplankton, *Diporeia* spp., and *Mysis* spp. Phytoplankton were collected by pumping water from the water column at the optimum depth for maximum phytoplankton density, zooplankton were collected in vertical tows, *Diporeia* spp. were collected in benthic tows, and *Mysis* spp. were collected in vertical and benthic tows (see Section 2.5.5 for details of the sample collection procedures). Lower pelagic food web samples were collected from 15 locations in Lake Michigan, including 9 stations within 4 designated biological sampling areas (biota boxes) and 6 additional routine monitoring stations (Table 7-1).

- **Chicago biota box** – a station in southern Lake Michigan basin near Chicago
- **Sturgeon Bay biota box** – a combination of three stations on the western side of the northern Lake Michigan basin near Sturgeon Bay, Wisconsin
- **Port Washington biota box** – a combination of two stations in the central Lake Michigan basin near Port Washington, Wisconsin
- **Saugatuck biota box** – a series of three stations on the eastern side of the southern Lake Michigan basin near Saugatuck, Michigan.

A total of 208 lower pelagic food web samples were collected and analyzed for *trans*-nonachlor, and 233 lower pelagic food web samples were collected and analyzed for PCBs (Table 7-1).

As noted in Chapter 2, there are 209 possible PCB congeners, and the investigators in this study reported results for 65 to 110 of these congeners, depending on the capabilities of each laboratory. The University of Minnesota determined results for 110 congeners or co-eluting congeners.

For the purposes of this report, we are presenting summaries of the results for the following subset of all of the analytes:

- PCB congener 33
- PCB congener 118
- PCB congener 180
- Total PCBs
- *trans*-nonachlor

Table 7-1. Number of Lower Pelagic Food Web Samples Analyzed for PCB Congeners and *trans*-Nonachlor

Sample Type	Sampling Locations		Sampling Dates	Number of Samples Analyzed for *trans*-Nonachlor	Number of Samples Analyzed for PCB Congeners and Total PCBs
Diporeia	Chicago biota box	5	06/26/94 to 10/10/95	6	6
	Sturgeon Bay biota box	40	06/18/94 to 09/23/95	5	5
		180	08/10/94 to 09/22/95	4	4
	Port Washington biota box	240	06/21/94 to 10/02/95	5	5
		280	06/21/94 to 10/01/95	6	6
	Saugatuck biota box	340	06/25/94 to 10/06/95	6	6
		380	06/25/94 to 10/06/95	6	6
	Other	47M	06/17/94 to 06/17/94	1	1
			Total	39	39
Mysis	Chicago biota box	5	06/26/94 to 10/10/95	6	6
	Sturgeon Bay biota box	140	06/18/94 to 09/23/95	6	6
		180	08/10/94 to 09/22/95	5	5
	Port Washington biota box	240	06/21/94 to 10/02/95	6	6
		280	06/21/94 to 10/01/95	6	6
	Saugatuck biota box	340	06/25/94 to 10/06/95	6	6
		380	06/24/94 to 10/06/95	6	6
	Other	18M	06/22/94 to 10/09/95	5	6
		27M	08/09/95 to 08/09/95	1	1
		47M	06/17/94 to 09/19/95	5	5
			Total	52	53
Phytoplankton	Chicago biota box	5	06/26/94 to 10/10/95	7	7
	Sturgeon Bay biota box	110	06/19/94 to 09/23/95	6	6
		140	06/18/94 to 09/23/95	6	6
		180	06/18/94 to 09/22/95	6	6
	Port Washington biota box	240	06/21/94 to 10/02/95	6	6
		280	06/21/94 to 10/01/95	5	6
	Saugatuck biota box	310	06/26/94 to 10/08/95	6	6
		340	06/25/94 to 10/06/95	6	6
		380	06/24/94 to 10/06/95	7	7
	Other	18M	06/22/94 to 10/09/95	6	6
		23M	06/23/94 to 06/23/94	1	1
		27M	06/20/94 to 06/20/94	1	1
		41	06/18/94 to 06/18/94	1	1
		47M	06/17/94 to 09/19/95	6	6
			Total	70	71

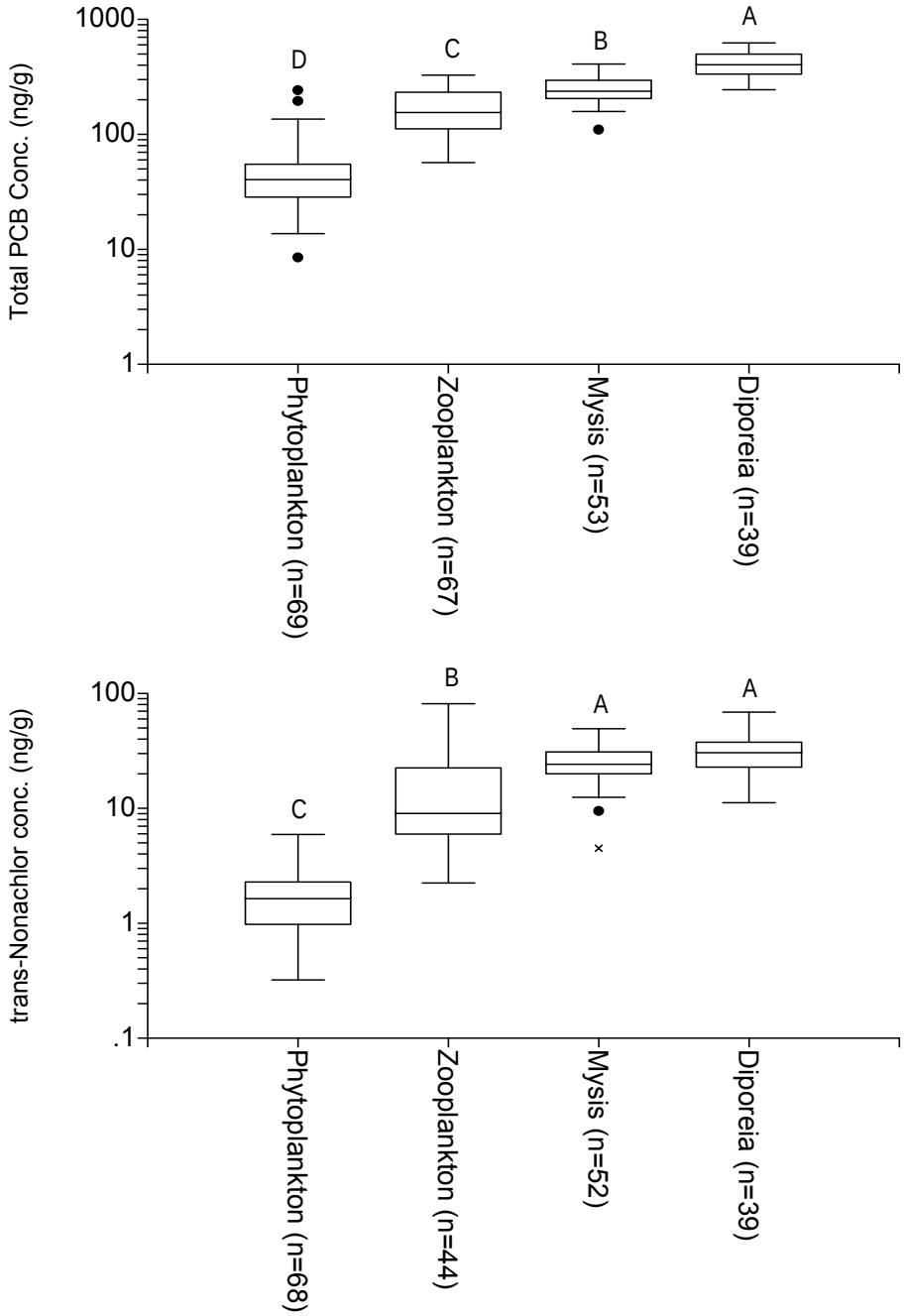
Sample Type	Sampling Locations		Sampling Dates	Number of Samples Analyzed for *trans*-Nonachlor	Number of Samples Analyzed for PCB Congeners and Total PCBs
Zooplankton	Chicago biota box	5	06/26/94 to 10/10/95	7	7
	Sturgeon Bay biota box	110	06/19/94 to 09/23/95	5	6
		140	06/18/94 to 09/23/95	5	6
		180	06/18/94 to 09/22/95	5	6
	Port Washington biota box	240	06/21/94 to 10/02/95	5	6
		280	06/21/94 to 10/01/95	2	6
	Saugatuck biota box	310	06/26/94 to 10/08/95	6	6
		340	06/25/94 to 10/06/95	5	6
		380	06/25/94 to 10/06/95	2	7
	Other	18M	06/22/94 to 10/09/95	1	6
		27M	06/20/94 to 06/20/94	1	1
		47M	06/17/94 to 09/19/95	2	6
		19M	01/24/95 to 01/24/95	1	1
	Total			47	70
Total				208	233

7.1.1 Sample Type and Species Variation

PCB and *trans*-nonachlor concentrations measured in the lower pelagic food web differed significantly among phytoplankton, zooplankton, *Mysis* spp., and *Diporeia* spp. samples (Figure 7-1). Concentrations of PCB 33, PCB 118, PCB 180, total PCBs, and *trans*-nonachlor were highest in samples of *Diporeia* spp., followed by *Mysis* spp., zooplankton, and phytoplankton, respectively (Table 7-2). Total PCB concentrations were 9 times higher in *Diporeia* spp. than in phytoplankton, averaging 420, 250, 170, and 49 ng/g dry weight in *Diporeia* spp., *Mysis* spp., zooplankton, and phytoplankton samples, respectively. *Trans*-Nonachlor concentrations were 19 times higher in *Diporeia* spp. than in phytoplankton, averaging 32, 25, 16, and 1.7 ng/g dry weight in *Diporeia* spp., *Mysis* spp., zooplankton, and phytoplankton samples, respectively.

A portion of the difference in PCB and *trans*-nonachlor concentrations among lower pelagic food web sample types is likely due to variations in the lipid content of the samples. Hydrophobic organic contaminants such as PCBs and *trans*-nonachlor preferentially concentrate in the fatty tissues of organisms, so those organisms with higher lipid content will likely concentrate more of these contaminants. This is evidenced by the fact that lipid content was positively correlated with total PCB and *trans*-nonachlor concentrations (r^2 of 0.25 for total PCB and 0.40 for *trans*-nonachlor), and the lipid content of phytoplankton was significantly lower than for the other sample types. The differences in lipid content among the sample types, however, explained only a quarter to less than half of the variability in total PCB and *trans*-nonachlor concentrations. Even when total PCB and *trans*-nonachlor concentrations were normalized by lipid content, the trends in PCB and *trans*-nonachlor concentrations among the sample types were almost always the same (Figure 7-2). Normalized total PCB and *trans*-nonachlor concentrations in *Diporeia* spp. and *Mysis* spp. were significantly higher than in zooplankton and phytoplankton, and normalized *trans*-nonachlor concentrations in zooplankton were significantly higher than in phytoplankton. Normalized total PCB concentrations in zooplankton, however, were not significantly different than in phytoplankton.

Figure 7-1. Total PCB and *trans*-Nonachlor Concentrations in the Lower Pelagic Food Web

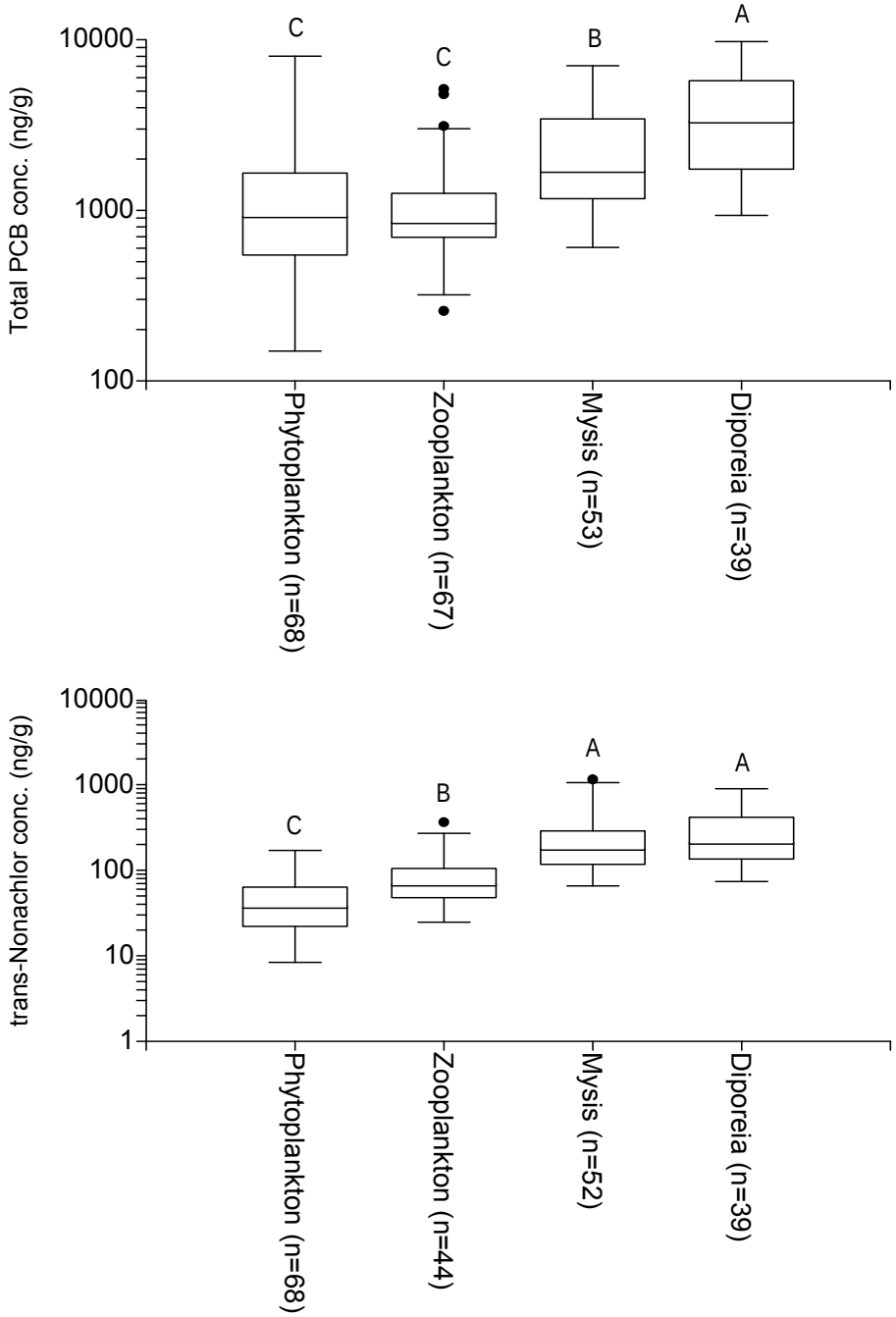


Boxes represent the 25th percentile (bottom of box), 50th percentile (center line), and 75th percentile (top of box) results. Bars represent the results nearest 1.5 times the inter-quartile range (IQR=75th-25th percentile) away from the nearest edge of the box. Circles represent results beyond 1.5*IQR from the box. The Xs represent results beyond 3*IQR from the box. The letters (A - D) above the boxes represent the results of the analysis of variance and multiple comparisons test. Boxes with the same letter were not statistically different (at alpha = 0.05). Concentration is plotted on a log scale.

Table 7-2. Mean Concentrations of PCBs and *trans*-Nonachlor Measured in the Lower Pelagic Food Web

Analyte	Sample Type	N	Mean (ng/g)	Range (ng/g)	SD (ng/g)	RSD (%)	Below DL (%)
PCB 33	*Diporeia*	39	0.99	0 to 3.0	0.76	77	5.1
	Mysis	53	0.64	0 to 5.0	0.85	130	15
	Phytoplankton	71	0.27	0 to 2.8	0.37	130	9.9
	Zooplankton	70	0.53	0 to 2.2	0.59	110	24
PCB 118	*Diporeia*	39	15	8.6 to 36	5.2	34	0
	Mysis	53	13	6.3 to 28	3.6	29	0
	Phytoplankton	71	1.6	0.20 to 10	1.5	97	0
	Zooplankton	70	5.5	0.072 to 20	3.4	63	0
PCB 180	*Diporeia*	39	17	6.4 to 49	7.3	43	0
	Mysis	53	9.4	3.1 to 18	3.4	36	0
	Phytoplankton	71	1.4	0.11 to 7.2	1.2	87	0
	Zooplankton	70	6.3	0.35 to 18	4.0	63	0
Total PCBs	*Diporeia*	39	420	240 to 620	100	24	0
	Mysis	53	250	110 to 410	61	24	0
	Phytoplankton	71	49	8.5 to 240	38	76	0
	Zooplankton	70	170	57 to 330	74	44	0
trans-Nonachlor	*Diporeia*	39	32	11 to 69	12	38	0
	Mysis	52	25	4.5 to 49	9.3	37	0
	Phytoplankton	70	1.7	0 to 5.9	1.0	60	2.9
	Zooplankton	47	16	2.2 to 81	16	100	0

Figure 7-2. Normalized (by Lipid Content) Total PCB and *trans*-Nonachlor Concentrations in the Lower Pelagic Food Web



Boxes represent the 25th percentile (bottom of box), 50th percentile (center line), and 75th percentile (top of box) results. Bars represent the results nearest 1.5 times the inter-quartile range (IQR=75th-25th percentile) away from the nearest edge of the box. Circles represent results beyond 1.5*IQR from the box. The letters (A - D) above the boxes represent the results of the analysis of variance and multiple comparisons test. Boxes with the same letter were not statistically different (at alpha = 0.05). Concentration is plotted on a log scale.

7.1.2 Seasonal Variation

The lower pelagic food web was sampled in six separate cruises in June 1994, August 1994, October 1994, March 1995, August 1995, and September 1995. Two-way analysis of variance revealed that total PCB concentrations in *Mysis* spp., zooplankton, and phytoplankton differed significantly by station and by sampling cruise. Seasonal and geographical variations, however, were small in comparison to differences due to sample type (phytoplankton, zooplankton, *Mysis* spp., and *Diporeia* spp.). Figure 7-3 shows the seasonal variation in total PCB concentrations by sample type. While there were no absolute seasonal trends in total PCB concentrations, average concentrations across stations were often higher in the spring and early summer (June 1994 and March 1995) than in the late summer (August 1994, August 1995, and September 1995). Total PCB concentrations in *Mysis* spp. samples were significantly higher in June 1994 and March 1995 than in August 1995. In zooplankton samples, total PCB concentrations were significantly higher in March 1995 and October 1994 than in either of the August cruises (August 1994 and August 1995). In phytoplankton samples, total PCB concentrations were significantly higher in June 1994 than in August 1994. Total PCB concentrations in *Diporeia* spp. did not differ significantly among cruises.

trans-Nonachlor concentrations in all lower pelagic food web sample types differed significantly by station and by sampling cruise. Figure 7-4 shows the seasonal variation in *trans*-nonachlor concentrations by sample type. Similarly to total PCB concentrations, *trans*-nonachlor concentrations for some sample types were often higher in the spring and early summer than in the late summer. In phytoplankton samples, *trans*-nonachlor concentrations were significantly higher in March 1995 than in September 1995 and significantly higher in June 1994 than in August 1994, October 1994, August 1995 or September 1995. In zooplankton samples, *trans*-nonachlor concentrations were significantly higher in March 1995 than in all other cruises. *trans*-Nonachlor concentrations in *Mysis* spp. samples were significantly higher in June 1994, October 1994, and March 1995 than in September 1995. *Diporeia* spp. samples did not fit the general trend of higher *trans*-nonachlor concentrations in spring and early summer than in late summer. The only significant differences between *trans*-nonachlor concentrations in *Diporeia* spp. samples were between the September 1995 and the August 1994 cruises.

Figure 7-3. Seasonal Variation of Total PCB Concentrations Measured in the Lower Pelagic Food Web of Lake Michigan

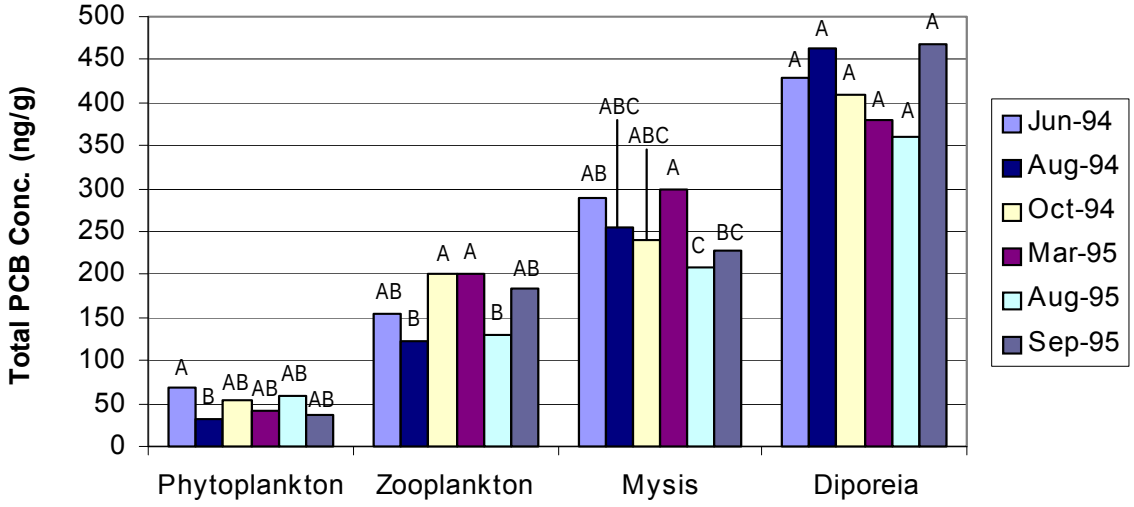
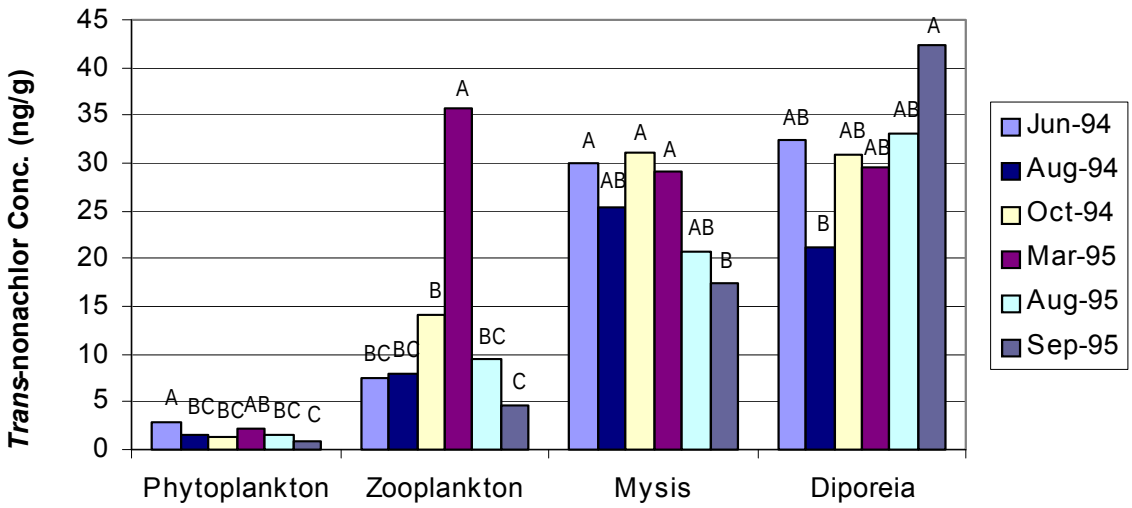


Figure 7-4. Seasonal Variation in *trans*-Nonachlor Concentrations Measured in the Lower Pelagic Food Web of Lake Michigan



7.1.3 Geographical Variation

Sampling of the lower pelagic food web was focused in the following four biological sampling areas or biota boxes:

- **Chicago biota box** – a station in southern Lake Michigan basin near Chicago
- **Sturgeon Bay biota box** – a combination of three stations on the western side of the northern Lake Michigan basin near Sturgeon Bay, Wisconsin
- **Port Washington biota box** – a combination of two stations in the central Lake Michigan basin near Port Washington, Wisconsin
- **Saugatuck biota box** – a series of three stations on the eastern side of the southern Lake Michigan basin near Saugatuck, Michigan.

In addition to focused sampling in these areas, samples also were collected from six routine monitoring sites throughout the lake (Table 7-1). Table 7-3 shows the concentrations of total PCBs measured in lower pelagic food web samples collected from the various sampling locations.

Table 7-3. Mean Concentrations of Total PCBs Measured in the Lower Pelagic Food Web at Various Sampling Locations

Sample Type	Sampling Location	N	Mean (ng/g)	Range (ng/g)	SD (ng/g)	RSD (%)	Below DL (%)
Diporeia	Chicago biota box	6	450	290 to 590	110	24	0
	Sturgeon Bay biota box	9	350	250 to 470	82	23	0
	Port Washington biota box	11	440	290 to 620	110	25	0
	Saugatuck biota box	12	440	240 to 560	90	21	0
	47M	1	340	NA	NA	NA	0
Mysis	Chicago biota box	6	200	110 to 330	82	40	0
	Sturgeon Bay biota box	11	250	180 to 320	52	21	0
	Port Washington biota box	12	230	190 to 270	24	10	0
	Saugatuck biota box	12	300	190 to 410	54	18	0
	18M	6	250	190 to 320	45	18	0
	27M	1	180	NA	NA	NA	0
	47M	5	250	160 to 410	93	37	0
Phytoplankton	Chicago biota box	7	55	35 to 100	24	43	0
	Sturgeon Bay biota box	18	40	14 to 140	27	68	0
	Port Washington biota box	12	41	22 to 63	13	32	0
	Saugatuck biota box	19	72	14 to 240	59	82	0
	18M	6	34	8.5 to 88	28	83	0
	23M	1	44	NA	NA	NA	0
	27M	1	49	NA	NA	NA	0
	41	1	52	NA	NA	NA	0
	47M	6	35	27 to 46	7.8	22	0
Zooplankton	Chicago biota box	7	180	110 to 270	62	35	0
	Sturgeon Bay biota box	18	110	57 to 270	59	56	0
	Port Washington biota box	12	180	83 to 300	59	33	0
	Saugatuck biota box	19	200	87 to 310	66	33	0
	18M	6	220	140 to 270	56	25	0
	27M	1	140	NA	NA	NA	0
	47M	6	170	110 to 330	93	53	0
	19M	1	280	NA	NA	NA	0

NA = Not applicable. Summary statistics could not be calculated for a single data point.

Among the biota boxes total PCB concentrations were generally highest at the Saugatuck biota box and lowest at the Sturgeon Bay biota box. Average total PCB concentrations in *Mysis* spp., phytoplankton, and zooplankton were higher at the Saugatuck biota box than all other biota boxes, and average total PCB concentrations in *Diporeia* spp., phytoplankton, and zooplankton were lower at the Sturgeon Bay biota box than all other biota boxes. These differences were not statistically significant for all cases, but two-

way analysis of variance (accounting for sampling station and sampling cruise) revealed that total PCB concentrations in two of the four lower pelagic food web sample types differed significantly. Total PCB concentrations in *Mysis* spp. were significantly higher at the Saugatuck biota box than at the Chicago biota box or Port Washington biota box, and total PCB concentrations in zooplankton were significantly lower at the Sturgeon Bay biota box than all other stations. This trend is consistent with the distribution of PCBs in Lake Michigan sediments (see Chapter 6). PCBs accumulated in the eastern side of the southern Lake Michigan basin, near Saugatuck, and were lower along the western shore and northern basin, near Sturgeon Bay.

The trend of increased concentrations near the Saugatuck biota box and decreased concentrations near the Sturgeon Bay biota box that was observed for total PCBs was not observed for *trans*-nonachlor accumulation in the lower pelagic food web (Table 7-4). Average *trans*-nonachlor concentrations in *Mysis* spp. were highest at the Saugatuck biota box, but concentrations in phytoplankton and zooplankton were highest at the Chicago biota box, and concentrations in *Diporeia* spp. were highest at the Port Washington biota box. Average *trans*-nonachlor concentrations were lowest at the Sturgeon Bay, Chicago, Port Washington, and Sturgeon Bay biota boxes for *Diporeia* spp., *Mysis* spp., phytoplankton, and zooplankton, respectively. Two-way analysis of variance revealed that differences in *trans*-nonachlor concentrations among sites were significant for *Mysis* spp. and zooplankton samples. *trans*-Nonachlor concentrations in *Mysis* spp. were significantly higher in Saugatuck and Sturgeon Bay biota boxes than in the Chicago biota box. *trans*-Nonachlor concentrations in zooplankton were significantly higher in the Port Washington biota box than the Sturgeon Bay biota box.

The observed trend of *trans*-nonachlor accumulation in the lower pelagic food web was also consistent with the geographical distribution of *trans*-nonachlor in sediments. *tran*s-Nonachlor was not preferentially accumulated in sediments along the eastern side of the southern basin (near the Saugatuck biota box) as was the case for total PCBs (see Chapter 6). Rather, accumulation of *trans*-nonachlor in Lake Michigan sediments was concentrated towards the center of the southern and central basins. Consistent with these findings, *trans*-nonachlor was not generally higher at Saugatuck than at Sturgeon Bay. In addition, *trans*-nonachlor in two of the sample types (*Diporeia* spp. and zooplankton) was higher at the Port Washington biota box (which is in the center of the lake) than either the Saugatuck or Sturgeon Bay biota boxes.

Table 7-4. Mean Concentrations of *trans*-Nonachlor Measured in the Lower Pelagic Food Web at Various Sampling Locations

Sample Type	Sampling Location	N	Mean (ng/g)	Range (ng/g)	SD (ng/g)	RSD (%)	Below DL (%)
Diporeia	Chicago biota box	6	31	19 to 49	10	32	0
	Sturgeon Bay biota box	9	29	19 to 51	10	35	0
	Port Washington biota box	11	38	19 to 69	15	40	0
	Saugatuck biota box	12	30	11 to 46	11	38	0
	47M	1	27	NA	NA	NA	0
Mysis	Chicago biota box	6	17	4.5 to 27	7.9	47	0
	Sturgeon Bay biota box	11	27	9.5 to 49	11	40	0
	Port Washington biota box	12	22	12 to 39	7.4	33	0
	Saugatuck biota box	12	30	13 to 46	10	33	0
	18M	5	28	21 to 34	5.2	18	0
	27M	1	19	NA	NA	NA	0
	47M	5	25	20 to 33	5.4	22	0
Phytoplankton	Chicago biota box	7	2.3	1.0 to 3.6	0.97	42	0
	Sturgeon Bay biota box	18	1.6	0.60 to 3.7	0.87	54	0
	Port Washington biota box	11	1.4	0.0 to 2.5	0.89	63	18
	Saugatuck biota box	19	1.8	0.71 to 3.4	0.77	44	0
	18M	6	1.8	0.46 to 5.9	2.1	120	0
	23M	1	2.0	NA	NA	NA	0
	27M	1	3.9	NA	NA	NA	0
	41	1	2.3	NA	NA	NA	0
	47M	6	1.3	0.32 to 2.8	0.86	65	0
Zooplankton	Chicago biota box	7	24	2.2 to 81	27	108	0
	Sturgeon Bay biota box	15	8.9	2.3 to 25	6.7	75	0
	Port Washington biota box	7	21	6.3 to 59	19	89	0
	Saugatuck biota box	13	13	2.2 to 29	9.8	77	0
	18M	1	45	NA	NA	NA	0
	27M	1	9.3	NA	NA	NA	0
	47M	2	31	7.8 to 54	32	105	0
	19M	1	34	NA	NA	NA	0

NA = Not applicable. Summary statistics could not be calculated for a single data point.

7.1.4 Bioaccumulation

Persistent organic pollutants, such as PCBs and *trans*-nonachlor, typically accumulate in living organisms above concentrations found in the water. This accumulation is due to the preferred partitioning of hydrophobic organic contaminants in organic tissues (such as lipids) over water, uptake from food, and/or reduced metabolism and elimination of persistent contaminants. The degree of accumulation is often quantified by a bioaccumulation factor, which is the ratio of the concentration of pollutant in an organism to the concentration of that pollutant in the water. When pollutants are increasingly accumulated with each trophic level of a food chain (or biomagnified), a biomagnification factor can be used to quantify the degree of accumulation from one trophic level to the next. A biomagnification factor is the ratio of the concentration of pollutant in organisms at a particular trophic level to the concentration of that pollutant in the next lowest trophic level.

To evaluate the degree of accumulation of PCBs and *trans*-nonachlor in the lower pelagic food web of Lake Michigan, bioaccumulation factors were calculated for each sample type (Table 7-5). Bioaccumulation factors were calculated as the mean concentration in a lower pelagic food web sample type divided by the lake-wide mean concentration in Lake Michigan. Concentrations of total PCBs in the lower pelagic food web were generally 10^5 to 10^6 times higher than dissolved concentrations of total PCBs in Lake Michigan water, which averaged 0.18 ng/L (or 0.00018 ng/g assuming a water density of 1g/mL). Bioaccumulation factors for total PCBs from water to the lower pelagic food web were 2.3 x 10^6, 1.4 x 10^6, 2.7 x 10^5, and 9.3 x 10^5 for *Diporeia* spp., *Mysis* spp., phytoplankton, and zooplankton, respectively. On a congener-specific basis, bioaccumulation factors were generally lower for the less-chlorinated PCB congeners and higher for the more-chlorinated congeners. Bioaccumulation factors for PCB 33 ranged from 3.0 x 10^4 to 1.1 x 10^5, while bioaccumulation factors for PCB 180 ranged from 2.9 x 10^6 to 3.5 x 10^7.

Table 7-5. Bioaccumulation Factors for PCBs and *trans*-Nonachlor in the Lower Pelagic Food Web

Analyte	*Diporeia*	*Mysis*	Phytoplankton	Zooplankton
PCB 33	1.1 x 10^5	7.1 x 10^4	3.0 x 10^4	5.8 x 10^4
PCB 118	6.2 x 10^6	5.1 x 10^6	6.5 x 10^5	2.2 x 10^6
PCB 180	3.5 x 10^7	1.9 x 10^7	2.9 x 10^6	1.3 x 10^7
Total PCBs	2.3 x 10^6	1.4 x 10^6	2.7 x 10^5	9.3 x 10^5
trans-Nonachlor	5.5 x 10^6	4.4 x 10^6	3.0 x 10^5	2.8 x 10^6

The accumulation of *trans*-nonachlor was slightly greater than the accumulation of total PCBs in the lower pelagic food web. Bioaccumulation factors for *trans*-nonachlor were 5.5 x 10^6, 4.4 x 10^6, 3.0 x 10^5, and 2.8 x 10^6 for *Diporeia* spp., *Mysis* spp., phytoplankton, and zooplankton, respectively.

To evaluate the accumulation and transfer of PCBs and *trans*-nonachlor between trophic levels within the lower pelagic food web, biomagnification factors also were calculated. Biomagnification factors between primary producers and primary consumers were calculated as the concentration of contaminants in *Diporeia* spp., *Mysis* spp., or zooplankton divided by the concentration in phytoplankton. Total PCB biomagnification factors were 8.5, 5.1, and 3.4 for *Diporeia* spp., *Mysis* spp., and zooplankton, respectively (Table 7-6). Higher bioaccumulation and biomagnification factors for *Diporeia* spp. could be due to specific life history characteristics including this organism's close association with sediments, which contained approximately 100,000 times the concentration of PCBs in water and slightly higher concentrations of PCBs than phytoplankton. Bioaccumulation factors for *Diporeia* spp. compared to sediments were 8.3 for total PCBs and 59 for *trans*-nonachlor.

Similar to bioaccumulation factors, biomagnification factors increased with increasing chlorination of PCB congeners. Biomagnification factors ranged from 1.9 to 3.6 for PCB 33, and from 4.5 to 12 for PCB 180 (Table 7-6). For *trans*-nonachlor, biomagnification factors were 18, 15, and 9.5 in *Diporeia* spp., *Mysis* spp., and zooplankton, respectively.

Table 7-6. Biomagnification Factors for PCBs and *trans*-Nonachlor between Primary Producers and Primary Consumers

Analyte	*Diporeia* / Phytoplankton	*Mysis* / Phytoplankton	Zooplankton / Phytoplankton
PCB 33	3.6	2.4	1.9
PCB 118	9.6	7.9	3.4
PCB 180	12	6.7	4.5
Total PCBs	8.5	5.1	3.4
trans-Nonachlor	18	15	9.5

7.2 Quality Implementation and Assessment

As described in Section 1.5.5, the LMMB QA program prescribed minimum standards to which all organizations collecting data were required to adhere. The quality activities implemented for the PCBs and *trans*-nonachlor monitoring portion of the study are further described in Section 2.7 and included use of SOPs, training of laboratory and field personnel, and establishment of MQOs for study data. A detailed description of the LMMB quality assurance program is provided in *The Lake Michigan Mass Balance Study Quality Assurance Report* (USEPA, 2001b). A brief summary of the quality of lower pelagic food web PCB and *trans*-nonachlor data is provided below.

Quality Assurance Project Plans (QAPPs) were developed by the PIs and were reviewed and approved by GLNPO. Each researcher trained field personnel in sample collection SOPs prior to the start of the field season and analytical personnel in analytical SOPs prior to sample analysis. Each researcher submitted test electronic data files containing field and analytical data according to the LMMB data reporting standard prior to study data submittal. GLNPO reviewed these test data sets for compliance with the data reporting standard and provided technical assistance to the researchers. In addition, each researcher's laboratory was audited during an on-site visit at least once during the time LMMB samples were being analyzed. The auditors reported positive assessments and did not identify issues that adversely affected the quality of the data.

As discussed in Section 2.7, data verification was performed by comparing all field and QC sample results produced by each PI with their MQOs and with overall LMMB Study objectives. Analytical results were flagged when pertinent QC sample results did not meet acceptance criteria as defined by the MQOs. These flags were not intended to suggest that data were not useable; rather they were intended to caution the user about an aspect of the data that did not meet the predefined criteria. Table 7-7 provides a summary of flags applied to the lower pelagic food web PCB and *trans*-nonachlor data. The summary includes the flags that directly relate to evaluation of the MQOs to illustrate some aspects of data quality, but does not include all flags applied to the data to document sampling and analytical information, as discussed in Section 2.7. No results were qualified as invalid, thus all results are represented in the analysis of lower pelagic food web PCB and *trans*-nonachlor concentrations presented in this report.

Table 7-7. Summary of Routine Field Sample Flags Applied to Select PCB Congeners and *trans*-Nonachlor in the Lower Pelagic Food Web

Analyte	Flags								
	Contamination	Precision		Bias					Invalid
	FBK	FFD	FDL	FMS	FSS	LOB	HIB	FPC	INV
PCB 33	45% (104)	7% (16)	4% (9)	0	4% (9)	0	0	0	0
PCB 118	2% (4)	2% (4)	0	0	4% (9)	0	0	0	0
PCB 180	5% (12)	3% (7)	1% (2)	0	4% (9)	0	0	0	0
trans-Nonachlor	0	2% (5)	2% (5)	0	31% (65)	0	0	1% (3)	0

The number of routine field samples flagged is provided in parentheses. The summary provides only a subset of applied flags and does not represent the full suite of flags applied to the data.

FBK = Failed blank (A related blank had a measurable value above the established QC limit when the blank was analyzed using the same equipment and analytical method. Reported value may be suspect.)
FDL = Failed laboratory duplicate (A laboratory duplicate associated with this analysis failed the acceptance criteria. Validity of reported value may be compromised.)
FFD = Failed field duplicate (A field duplicate associated with this analysis failed the acceptance criteria. Validity of reported value may be compromised.)
FPC = Failed performance check (A laboratory performance check sample associated with this analysis failed the acceptance criteria. Validity of reported value may be compromised.)
FSS = Failed surrogate (Surrogate recoveries associated with this analysis failed the acceptance criteria. Validity of reported value may be compromised.)
FMS = Failed matrix spike (A matrix spike associated with this analysis failed the acceptance criteria. Validity of reported value may be compromised.)
LOB = Likely biased low (Reported value is probably biased low as evidenced by LMS (lab matrix spike) results, SRM (standard reference material) recovery or other internal lab QC data. Reported value is not considered invalid.)
HIB = Likely biased high (Reported value is probably biased high as evidenced by LMS (lab matrix spike) results, SRM (standard reference material) recovery, blank contamination, or other internal lab QC data. Reported value is not considered invalid.)
INV = Invalid (Reported value is deemed invalid by the QC Coordinator.)

PIs used surrogate spikes to monitor the bias of the analytical procedure. The PCB and *trans*-nonachlor results were corrected for the recoveries of the surrogates. Only 4% of PCB results were qualified for surrogate recovery problems (Table 7-7). For *trans*-nonachlor, 31% of results were qualified for surrogate recovery problems (FSS). Surrogate recoveries were below the lower QC bound of 50% in 6% of samples and above the upper QC bound of 125% in 25% of samples. The mean surrogate recovery for *trans*-nonachlor, however, was 109%. Laboratory matrix spike samples also were used to monitor analytical bias, and no results were qualified for failed matrix spikes. Based on an analysis of matrix spikes, standard reference material recovery, blank contamination, and other internal QC data, the QC coordinator did not qualify any samples as high or low biased. The QA report (USEPA, 2001b), however, did mention that PCB 99 was prone to chromatographic interference in the plankton media, which could lead to a potentially high bias for this congener and for total PCB values that contained a significant proportion from PCB 99.

Field blanks, consisting of glass fiber filters, were collected for PCBs and *trans*-nonachlor analysis. It was later determined that these glass fiber filter blanks were not representative of the plankton matrix, so results were not flagged based on the results of field blanks. Laboratory blanks, consisting of a volume of solvent processed through an empty Soxhlet apparatus in the same fashion used to extract the field samples, also were prepared and analyzed for PCBs and *trans*-nonachlor. PCB congeners were detected in all laboratory blanks analyzed. In accordance with the researcher's data qualifying rules, samples were flagged for a failed blank (FBK) if the mass of the detected congener in the blank was greater than 10% of the field sample mass or if the blank result was greater than the method detection limit. The level of contamination varied by PCB congener, with only 2% of PCB 118 results flagged for failed blanks, and with 45% of PCB 33 results flagged for failed blanks. Congeners 4+10, 31, 33, 44, 81, 87, 114+131, 123+149, 153, 158, and 170+190 were commonly detected in laboratory blanks. None of the field sample results for *trans*-nonachlor were qualified because of laboratory blank results.

Field duplicates were collected at frequencies of 8%, 17%, 21%, and 11% for *Diporeia* spp., *Mysis* spp., phytoplankton, and zooplankton, respectively. Laboratory duplicates were prepared and analyzed at a frequency of 8.1%. In accordance with the researcher's data qualifying rules for field and laboratory duplicates, samples were flagged for a failed duplicate (FFD or FDL) if the relative percent difference between duplicate results was greater than 30%. Only a small percentage of results (0 to 7% for *trans*-nonachlor and the PCB congeners evaluated) were qualified for failed field or laboratory duplicates.

As discussed in Section 1.5.5, MQOs were defined in terms of six attributes: sensitivity, precision, accuracy, representativeness, completeness, and comparability. GLNPO derived data quality assessments based on a subset of these attributes. For example, system precision was estimated as the mean relative percent difference (RPD) between the results for field duplicate pairs. Similarly, analytical precision was estimated as the mean RPD between the results for laboratory duplicate pairs. Table 7-8 provides a summary of data quality assessments for several of these attributes for the lower pelagic food web data.

Because the relative variability of most measurement techniques increases as one approaches the detection limit of the technique, the assessments of the system and analytical precision were divided into two concentration regimes. One measure of precision was calculated for those field and laboratory duplicate results that were less than five times the method detection limit (MDL) of the analyte, and a separate measure was calculated for those field and laboratory duplicate results that were greater than five times the MDL.

Table 7-8. Data Quality Assessment for Select PCB Congeners and *trans*-Nonachlor in Lower Pelagic Food Web Samples

Analyte/Number Field Samples	Parameter	Number of QC samples	Assessment
PCB 33 (233 samples)	System Precision - Mean Field Duplicate RPD (%), > 5 * MDL	24 field duplicate pairs	28%
	System Precision - Mean Field Duplicate RPD (%), < 5 * MDL	7 field duplicate pairs	87%
	Analytical Precision - Mean Lab Duplicate RPD (%), > 5 * MDL	12 lab duplicate pairs	39%
	Analytical Precision - Mean Lab Duplicate RPD (%), < 5 * MDL	5 lab duplicate pairs	90%
	Analytical Bias - Mean Lab Matrix Spike Recovery (%)	20 lab matrix spike samples	87%
	Analytical Sensitivity - Samples Reported as < MDL (%)	-	15%
PCB 118 (233 samples)	System Precision - Mean Field Duplicate RPD (%), > 5 * MDL	34 field duplicate pairs	16%
	Analytical Precision - Mean Lab Duplicate RPD (%), > 5 * MDL	19 lab duplicate pairs	12%
	Analytical Bias - Mean Lab Matrix Spike Recovery (%)	20 lab matrix spike samples	68%
	Analytical Sensitivity - Samples Reported as < MDL (%)	-	0%
PCB 180 (233 samples)	System Precision - Mean Field Duplicate RPD (%), > 5 * MDL	33 field duplicate pairs	23%
	Analytical Precision - Mean Lab Duplicate RPD (%), > 5 * MDL	19 lab duplicate pairs	13%
	Analytical Bias - Mean Lab Matrix Spike Recovery (%)	20 lab matrix spike samples	93%
	Analytical Sensitivity - Samples Reported as < MDL (%)	-	0%
trans-Nonachlor (208 samples)	System Precision - Mean Field Duplicate RPD (%), > 5 * MDL	29 field duplicate pairs	15%
	Analytical Precision - Mean Lab Duplicate RPD (%), > 5 * MDL	17 lab duplicate pairs	21%
	Analytical Bias - Mean Lab Matrix Spike Recovery (%)	14 lab matrix spike samples	77%
	Analytical Sensitivity - Samples Reported as < MDL (%)	-	0.5%

RPD = Relative percent difference
MDL = Method detection limit

System precision was relatively consistent among the PCB congeners evaluated. In samples with concentrations greater than five times the MDL, mean field duplicate RPDs were 28%, 16%, and 23% for PCB congeners 33, 118, and 180, respectively, indicating good precision. Similarly, the mean field duplicate RPD for *trans*-nonachlor was 15%. For samples with concentrations less than five times the MDL, precision was reduced, and the mean field duplicate RPD was 87% for PCB 33. For the remaining congeners presented, all duplicate sample results were greater than five times the MDL. Analytical precision was similar to system precision, and for two analytes, mean laboratory duplicate RPDs were higher than mean field duplicate RPDs. This could suggest that the majority of the variability associated with the measurement system for these analytes is due to the analytical component.

Analytical bias was evaluated by calculating the mean recovery of laboratory matrix spike samples (LMS). Results indicated a slight low bias overall for all analytes. Mean LMS recoveries were 87%, 68%, 93%, and 77% for PCB 33, PCB 118, PCB 180, and *trans*-nonachlor, respectively. The PI and QC coordinator determined, however, that the bias was not strong enough to warrant flagging the data as low biased (LOB).

Analytical sensitivity was evaluated by calculating the percentage of samples reported below the MDL. No PCB 118 or PCB 180 results were below the MDL, and only 0.5% of *trans*-nonachlor results were below the MDL. For PCB 33, 15% of sample results were reported below the MDL. Results from these samples were not censored and were used as reported in the analysis of lower pelagic food web contamination presented in this report.

7.3 Data Interpretation

7.3.1 Comparison to Historical Studies

In this study, total PCB concentrations in the lower pelagic food web averaged 420, 250, 170, and 49 ng/g for *Diporeia* spp., *Mysis* spp., zooplankton, and phytoplankton, respectively. Jackson *et al.* (1998) measured similar PCB concentrations in Lake Michigan biota in 1995 and found the same relative degree of contamination (plankton < *Mysis relicta* < *Diporeia* spp.). Jackson *et al.* (1998) measured an average total PCB concentration of 127 ng/g dry weight in the 63-243 μm size fraction of plankton and 118 ng/g in the 243+ μm size fraction, slightly less than measured for zooplankton in the LMMB Study, but Jackson *et al.* (1998) explained that the plankton samples contained both phytoplankton and zooplankton. Total PCB concentrations measured by Jackson *et al.* (1998) in *Mysis relicta* and *Diporeia* spp. averaged 354 and 1107 ng/g, respectively, and were higher than concentrations measured in the LMMB Study. Oliver and Niimi (1988) measured similar concentrations of PCBs in the lower pelagic food web of Lake Ontario. Total PCB concentrations averaged 50 ng/g in plankton, 330 ng/g in mysids, and 790 ng/g in amphipods.

Total PCB concentrations in the lower pelagic food web of Lake Michigan were lower than measured by other researchers in Lake Huron (Anderson *et al.*, 1982) and Green Bay (Willman *et al.*, 1999). Anderson *et al.* (1982) measured total PCB concentrations of 92 and 126 ng/g in two phytoplankton species, *Cladophora* and *Ulothrix*. In mixed plankton from Lake Huron, Anderson *et al.* (1982) measured 1651 ng/g of total PCBs, which is approximately 10 times the level measured in zooplankton from the LMMB Study and 34 times the level measured in phytoplankton from the LMMB Study. In Green Bay phytoplankton, Willman *et al.* (1999) measured total PCB concentrations of 115 to 640 ng/g, which is 2 to 13 times the level measured in Lake Michigan phytoplankton. Total PCB concentrations in Green Bay zooplankton ranged from 678 to 1670 ng/g and were 4 to 10 times the levels measured in Lake Michigan zooplankton. This could be explained by the relatively higher dissolved PCB concentrations in the water column of Green Bay compared to Lake Michigan. Willman *et al.* (1999) measured total PCB

concentrations of 2.87 to 4.67 ng/L in Green Bay water, which is an order of magnitude higher than average total PCB concentrations in Lake Michigan (see Chapter 5).

Total PCB concentrations in the lower pelagic food web of Lake Michigan were higher than measured by other researchers in Swiss lakes (Berglund *et al.*, 2000) and marine pelagic food webs (Harding *et al.*, 1997; Fisk *et al.*, 2001b). In 19 Swiss lakes, Berglund *et al.* (2000) measured mean total PCB concentrations of 28 and 33 ng/g in phytoplankton and zooplankton, respectively. Harding *et al.* (1997) measured total PCB concentrations of 0.5 to 147 ng/g in plankton from the southern Gulf of St. Lawrence, which is lower than the average concentration measured for zooplankton in the LMMB Study. Fisk *et al.* (2001b) also measured lower total PCB concentrations in high Arctic marine zooplankton, which averaged 30 ng/g total PCBs.

7.3.2 Seasonal Variation

In the LMMB Study, average PCB concentrations in the lower pelagic food web were often highest in the spring and early summer (March - June) and lowest in the late summer and fall (August - September). This finding agrees with the findings of Epplett *et al.* (2000), who found that concentrations of PCBs in plankton in Lake Erie varied seasonally, with peaks in the spring or early summer (primarily June) and decreasing concentrations throughout the summer. In the arctic marine environment, Hargrave *et al.* (2000) also found seasonal variations in planktonic total PCB concentrations. Total PCBs were maximized in the spring and early summer (May/June) and decreased in the late summer and fall (August/September). Hargrave *et al.* (2000) concluded that equilibrium occurs rapidly between plankton and water PCB concentrations. If finite amounts of dissolved PCBs are available for uptake, when planktonic biomass levels change, there must be a rapid equilibrium reflected in increasing or decreasing PCB concentrations. Hargrave *et al.* (2000) observed that the minimum PCB concentrations in plankton that occurred in July and August corresponded with high particulate organic carbon concentrations indicative of high production in the planktonic community.

Swackhamer and Skoglund (1993) and Stange and Swackhamer (1994) investigated uptake of PCBs by several phytoplankton species that were exposed to these contaminants under controlled conditions. The goals of these two studies included determining if kinetics or equilibrium partitioning of PCBs controlled the bioaccumulation of hydrophobic organic contaminants such as PCBs. Cultures of phytoplankton were exposed to a mixture of 40 PCB congeners that included representatives from all 10 levels of chlorination. Exposures were carried out for 20 and 40 days, respectively, with samples of phytoplankton and water collected at intervals throughout the study. PCB concentrations were measured in both the phytoplankton and the water, in order to estimate bioaccumulation rates and bioaccumulation factors (BAFs).

Swackhamer and Skoglund (1993) held separate phytoplankton cultures at 11°C and 20°C to simulate conditions that result in minimal algal growth (11°C) and average algal growth (20°C). The experiments at 11 °C were carried out for 20 days, with duplicate samples of both algae and water collected at 0.2 days, 1 day, 3 days, and 20 days. They found that there was a relationship between the uptake of PCBs and the growth rate of the phytoplankton. Under conditions of minimal growth (11°C), Swackhamer and Skoglund found that the uptake of PCBs was consistent with equilibrium partitioning between the water and lipids within the plankton cells. The logs of the calculated BAFs for the PCB congeners exhibited a linear relationship with the logs of the octanol-water partitioning coefficients (K_{ow}) for the contaminants, with the more highly chlorinated congeners taking longer to reach equilibrium than the less chlorinated congeners. However, even at 20 days, most of the congeners did not achieve equilibrium. Swackhamer and Skoglund noted their results differed from many reports in the literature that suggest that equilibrium is reached rapidly and that many modeling efforts assume that it is instantaneous.

Under the average growth conditions (20°C), however, there was no correlation between log BAF and log K_{ow} for most of the PCB congeners studied. Under these average growth conditions, only congeners with log K_{ow} values less than 5.5 (e.g., mono- through trichlorinated congeners) exhibited a correlation between log BAF and log K_{ow}. Swackhamer and Skoglund offered two possible explanations for the result under average growth conditions:

1. The kinetics of phytoplankton growth and contaminant uptake are of the same order. Thus, an increase in biomass (organism growth) dilutes the concentration of PCBs in the organism, resulting in a constant BAF over time.

2. Cellular metabolism increased during growth, leading to increased excretion of metabolic waste products, comprised mostly of dissolved organic carbon. Hydrophobic contaminants such as PCBs may associated with those metabolic waste products, and thus be excreted from the cells.

Stange and Swackhamer (1994) exposed phytoplankton cultures to the PCBs for 40 days at 11°C, in order to investigate PCB uptake under minimal growth conditions that favored equilibrium partitioning. The results of that study indicate that PCB uptake under these conditions is controlled by equilibrium partitioning. Stange and Swackhamer identified an additional factor that may control PCB uptake of the highly chlorinated congeners. The movement of those congeners through cell membranes (e.g., from the water into the organism) may depend on their stereochemistry, with PCBs containing three or four chlorine atoms in the *ortho* positions able to pass more easily through membranes into the cells. We note that this additional factor is consistent with the "structure-activity relationship" theory underlying the designation of 12 of the 209 PCB congeners as "toxic" (see Section 2.1.6).

The implications of the works of Swackhamer and Skoglund (1993) and Stange and Swackhamer (1994) or the LMMB Study are that the seasonal variations in PCB concentrations in the lower pelagic food web observed may be the result of the growth rates of phytoplankton species as well as patterns of dominance of different species during the course of the year. The high PCB concentrations in spring may reflect equilibrium partitioning processes that occur at colder water temperatures and low light conditions, while the low PCB concentrations in later summer and fall may reflect the increased growth of organisms in response to warmer water and increased daylight.

7.3.3 Bioaccumulation and Trophic Transfer

PCBs and *trans*-nonachlor significantly accumulated in the lower pelagic food web of Lake Michigan above concentrations in the water column. Bioaccumulation factors from water to the lower pelagic food web ranged from 10^5 to 10^6 for *trans*-nonachlor and from 10^4 to 10^7 for total PCBs depending on the PCB congener and the compartment (e.g., *Diporeia* spp., *Mysis* spp., phytoplankton, or zooplankton). This is similar to the bioaccumulation factors measured by other researchers. Willman *et al.* (1999) measured bioaccumulation factors of 10^4 to 10^6 in Green Bay plankton. Oliver and Niimi (1988) also measured bioaccumulation factors of 10^3 to 10^5 for plankton, 10^4 to 10^6 for Mysis, and 10^3 to 10^6 for amphipods in Lake Ontario.

Within the lower pelagic food web, PCB and *trans*-nonachlor concentrations differed significantly among the measured compartments. Concentrations were lowest in phytoplankton, at the base of the pelagic food web. At the next trophic level (Figure 7-5), zooplankton contained significantly higher levels of PCBs and *trans*-nonachlor. Total PCB concentrations increased by a factor of 3.4 in the trophic transfer from phytoplankton to zooplankton, and *trans*-nonachlor concentrations increased by a factor of 9.5 in this transfer. Other researchers have also measured significant increases in PCB concentrations from phytoplankton to zooplankton. Willman *et al.* (1999) measured biomagnification factors of 1 to 10 between phytoplankton and zooplankton for tetra-, penta-, and hexachlorobiphenyl congeners. Willman

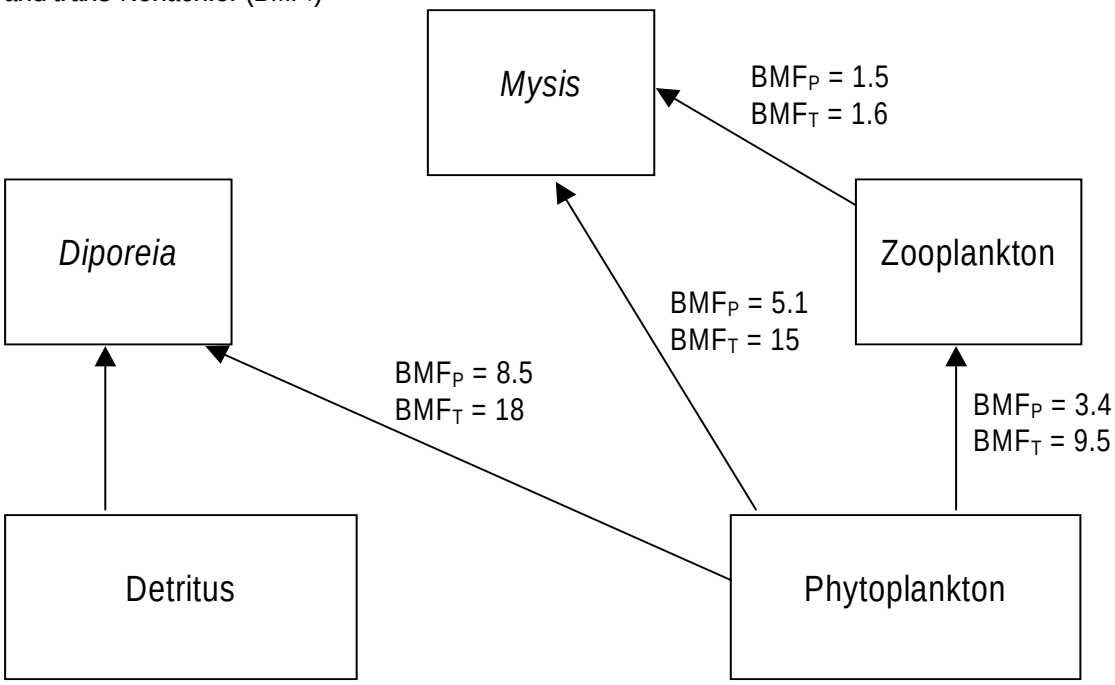
et al. (1999) found that the tri-, hepta-, and octachlorobiphenyl congeners accumulated to a lesser degree. Anderson *et al.* (1982) found approximately a 14 times increase in PCB concentrations from the phytoplankton, *Cladophora*, to zooplankton (>153-μm size range).

Other researchers have not found evidence of biomagnification of PCBs in the lower pelagic food web and have suggested that differences in PCB concentrations are explained by factors such as lipid content, age, size, or depuration rates. Berglund *et al.* (2000) did not find significant differences in total PCB concentrations between phytoplankton and zooplankton, and Harding *et al.* (1997) did not find significant differences in total PCB concentrations as plankton size varied (presumably accounting for differences between phytoplankton and zooplankton). If fact, Berglund *et al.* (2000) noted that when concentrations were normalized to lipid content, PCB concentrations in zooplankton were lower than in phytoplankton. In the LMMB Study, the same was true when PCB concentrations were normalized based on lipid content. Because the lipid content of zooplankton (19%) was substantially higher than for phytoplankton (4.8%), lipid normalized total PCB concentrations were only 1100 ng/g lipid in zooplankton compared to 1500 ng/g lipid in phytoplankton. In the LMMB Study, however, lipid content did not explain all observed differences in PCB and *trans*-nonachlor concentrations among the lower pelagic food web compartments. Lipid-normalized total PCB concentrations were still significantly higher in *Mysis* spp. and *Diporeia* spp. than in phytoplankton, and lipid-normalized *trans*-nonachlor was significantly higher in zooplankton, *Mysis* spp., and *Diporeia* spp. than in phytoplankton (Figure 7-2).

In addition to zooplankton, *Diporeia* spp. and *Mysis* spp. also occupy the second trophic level, however, trophic transfer from phytoplankton is less direct for these species (Figure 7-5). While *Diporeia* spp. feeds on phytoplankton, it is primarily a detrital feeder. *Mysis* spp. is a non-selective filter feeder that may feed on phytoplankton or zooplankton, such that this species may functionally occupy the second or third trophic levels. PCB and *trans*-nonachlor concentrations were significantly higher in *Mysis* spp. and *Diporeia* spp. than in phytoplankton or zooplankton on either a dry-weight basis (Figure 7-1) or a lipid-normalized dry weight basis (Figure 7-2). The higher concentrations of contaminants in *Diporeia* spp. may be indicative of trophic transfer from phytoplankton, but more likely is due to this organism's close association with the more heavily contaminated sediments. Even compared to sediments, however, *Diporeia* spp. significantly accumulated organic pollutants. Biota-sediment accumulation factors for *Diporeia* spp. were 8.3 for total PCBs and 59 for *trans*-nonachlor. Jackson *et al.* (1998) also suggested that *Diporeia* spp. was more representative of sediment contamination, while plankton were more representative of water column contamination.

Mysis spp. are less associated with detrital sediments than *Diporeia* spp., and accumulation in this species may be more directly linked to transfer through phytoplankton and zooplankton. Total PCB concentrations in *Mysis* spp. exceeded phytoplankton and zooplankton by factors of 5.1 and 1.5, respectively. *trans*-Nonachlor concentrations in *Mysis* spp. exceeded phytoplankton and zooplankton by factors of 15 and 1.6, respectively. Even when normalized to lipid content, *Mysis* spp. exceeded phytoplankton and zooplankton PCB concentrations significantly, by factors of 1.8 and 2.4, and lipid-normalized *trans*-nonachlor concentrations in *Mysis* spp. exceeded phytoplankton and zooplankton significantly by factors of 5.4 and 2.7. These results are similar to the total PCB biomagnification factor of 6.6 measured between plankton and *Mysis* by Oliver and Niimi (1988) in Lake Ontario. This factor varied from approximately 1 to 12 depending upon the specific PCB congener. Fisk *et al.* (2001a) also observed biomagnification from zooplankton to predatory invertebrates. Fisk *et al.* (2001a) calculated a biomagnification factor of 7.8 for total PCB transfer from *Calanus hyperboreus* (an herbaceous copepod) to *Themisto libellula* (a predatory amphipod), however, the authors noted that differences in concentrations at this low level of the food chain may be due to differences in organism size and may be more controlled by concentrations in water than in prey. The same factors could be controlling bioaccumulation of PCBs in *Mysis* in this study, since *Mysis* were considerably larger than the zooplankton species that were collected.

Figure 7-5. Lower Pelagic Food Web Structure and Biomagnification Factors for Total PCBs (BMF_P) and *trans*-Nonachlor (BMF_T)

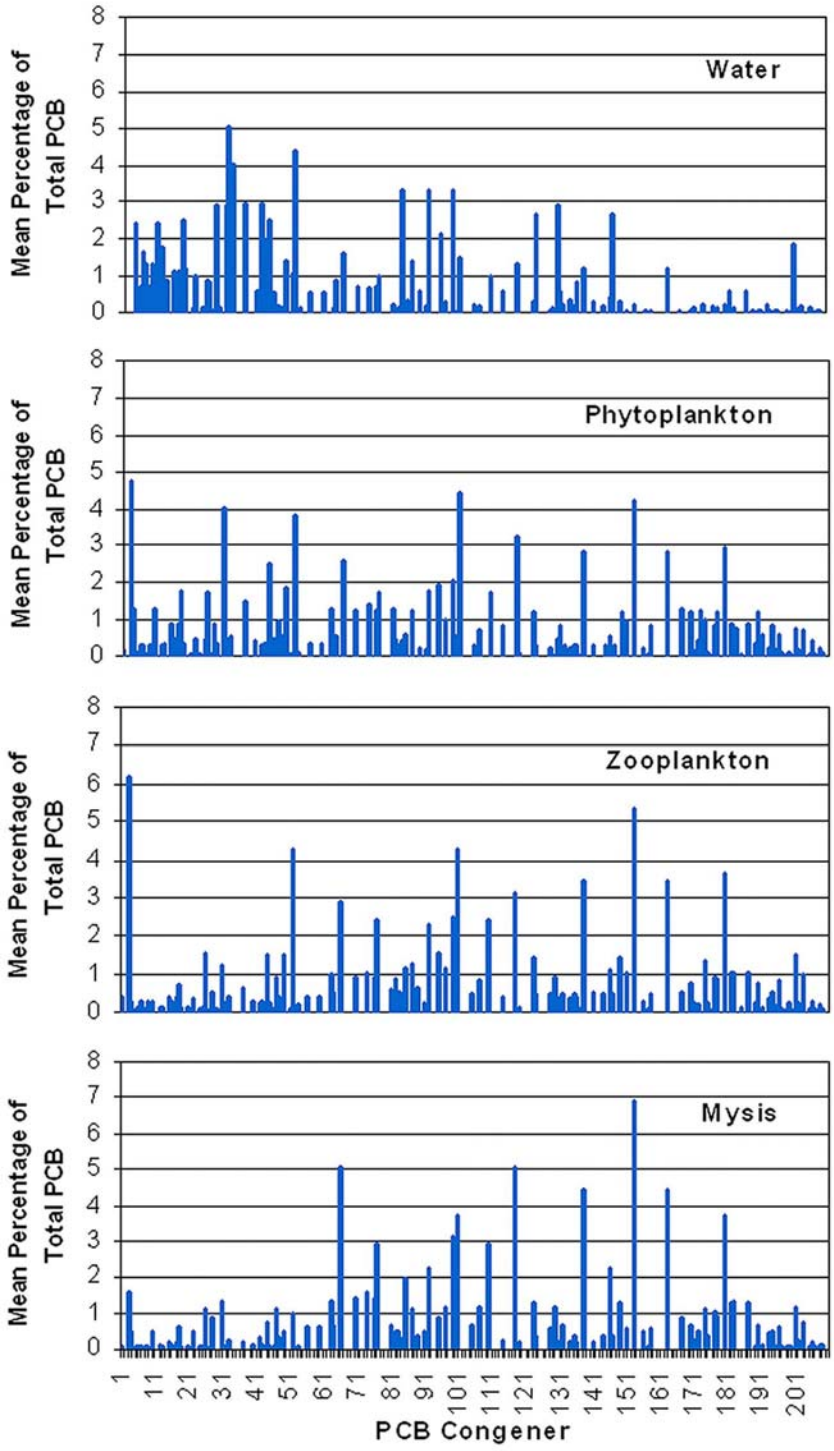


7.3.4 Fractionation

Throughout the lower pelagic food web, PCB congeners were accumulated differentially, with more highly chlorinated and more lipophilic congeners accumulated to a greater extent. For the three congeners specifically highlighted in this study (PCB 33, PCB 118, PCB 180), bioaccumulation factors generally increased by an order of magnitude from PCB 33 (a trichlorobiphenyl) to PCB 118 (a pentachlorobiphenyl) and another order of magnitude from PCB 118 to PCB 180 (a heptachlorobiphenyl) (Table 7-5). This differential accumulation of PCB congeners from water is expected based on the increasing octanol-water partition coefficients with increasing PCB chlorination. Researchers have described this relationship with linear regressions of log bioaccumulation factors versus log octanol-water partition coefficients (Mackay, 1982; Oliver and Niimi, 1988).

Not only did bioaccumulation factors increase with increasing chlorination of PCB congeners, but biomagnification factors also increased with increasing PCB chlorination. For example, biomagnification factors from phytoplankton to zooplankton increased from 1.9 to 3.4 to 4.5, for PCB congeners 33, 118, and 180, respectively (Table 7-6). While trends of increasing bioaccumulation factors and increasing biomagnification factors were observed for the three congeners specifically highlighted in this study, these trends were also generally true for all PCB congeners. Figure 7-6 shows the relative percentages of individual PCB congeners in water, phytoplankton, zooplankton, and *Mysis* spp. In water, there is a predominance of the less-chlorinated PCB congeners, and this predominance shifts progressively to more-chlorinated congeners with increasing trophic levels.

Figure 7-6. Mean Percentage of Individual PCB Congener Contribution to Total PCB Concentrations



The shift from less to more-chlorinated PCB congeners with increasing trophic level can be more easily observed when PCB congeners are grouped by chlorination level homologs (e.g., di-, tri-, tetra-, penta-, hexa-, hepta-, and octachlorobiphenyls). Figure 7-7 shows the percent change in the relative contribution (to total PCB concentration) of PCB congener homologs between compartments. Positive percent

changes indicate the relative enrichment of that homolog group between compartments, and negative percent changes indicate the relative depletion of that homolog group between compartments. In transfers from water to phytoplankton, the di- and trichlorobiphenyls are reduced in relative proportion to total PCBs, while the penta-, hexa-, and heptachlorobiphenyls are enriched. The same general trend is seen in the transfer from phytoplankton to zooplankton and the transfer from zooplankton to *Mysis*.

Other researchers have observed this same trend. Jackson *et al.* (1998) found a relative shift from less-chlorinated PCB congeners in the plankton to more-chlorinated PCB congeners in *Mysis relicta* and *Diporeia* spp. Oliver and Niimi (1988) also observed differential PCB fractionation from water to plankton to mysids. Less-chlorinated PCB congeners comprised a higher fraction of total PCBs in water than in higher trophic levels. Similar to the LMMB Study, Willman *et al.* (1997) found that the penta-, hexa-, and heptachlorobiphenyl congeners were enriched relative to other congeners as PCBs moved to higher trophic levels from sediments to plankton to fish.

Figure 7-7. Relative Enrichment or Depletion of PCB Congener Homolog Groups between Compartments